

## One-Phase Preparation of Palladium Nanoparticles Using Thiol-Functionalized Ionic Liquid

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**Abstract**—Thiol-functionalized ionic liquid (TFIL: 1,3-di(2',3'-dimercaptoacetoxypropyl) imidazolium, 3''-mercapto-1''-propanesulfonic acid) as a stabilizer for preparing palladium (Pd) nanoparticles was synthesized. The suggested TFIL was designed to have thiol groups on both cation and anion as well as on symmetrical positions in cation. Transmission electron microscopy (TEM) shows that the average diameter of the palladium nanoparticles was 3.0 nm and that the standard deviation was 0.15 nm. The overall results strongly suggest that this potential TFIL can act as a highly effective stabilizer for the preparation of Pd nanoparticles.

Key words: Palladium Nanoparticle, Thiol-Functionalized Ionic Liquid, Ionic Liquid, TEM

### INTRODUCTION

Ionic liquids (ILs) have received growing attention for academic and industrial applications, and their new applications have also appeared in several important fields [Kim et al., 2004a, b, c, d, e; Marsh et al., 2002; Demberelnyamba et al., 2004] and will continue to expand to numerous technologies. Basically, ILs comprise cations and anions, and can be synthesized in an endless number of ways according to the combination of cations and anions. It must be furthermore recognized that their physical and thermal properties depend strongly on the species of cation and anion as well as on the length of the alkyl groups of cation [Marsh et al., 2002].

The ILs based on imidazolium cation are especially favorable for green industrial applications. Their hydrophilic or hydrophobic properties of air and water stability, high conductivity, and wide potential windows make the ILs as potential candidates that can be used for reaction media and batteries [Ngo et al., 2000; Kim et al., 2004a]. These unique properties are expected to possess easily accessible and highly valuable information that can be utilized as the firm criteria of target ILs. However, most of researches associated with various IL applications have mainly focused on 1,3-dialkylimidazolium salts, even though an enormous number of ILs have been newly reported.

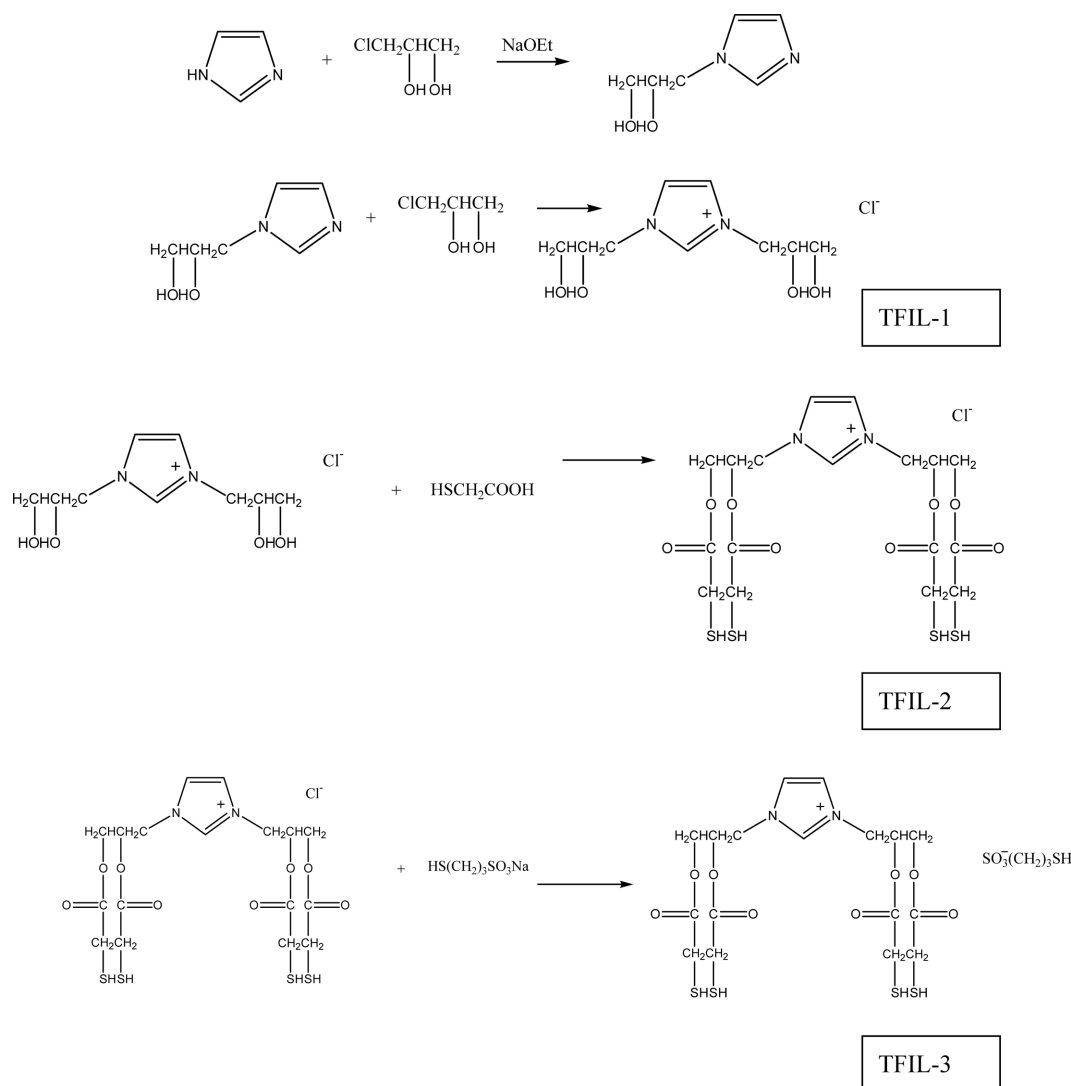
The current interest in transition metal nanoparticles is to prepare size-selective nanoparticles because their physical properties change with their nano-scale size. Polymers, micelles, and coordinative ligands, which have been widely used as stabilizers, generate characteristic properties by manipulating the size of these materials [Yonezawa et al., 1995]. Brust and co-workers developed a facile synthesis method of alkanethiol-stabilized gold nanoparticles [Burst et al., 1994]. To closely examine the general characteristics of metal nanoparticles, special emphasis was given to gold (Au), platinum (Pt), and palladium (Pd) nanoparticles stabilized by thiol functional groups.

Particles synthesized in organic solvents are water-immiscible, which limits their applicability. Many applications require for nanoparticles to be dispersible and stable in water. However, water-based syntheses of nanoparticles are fraught with many problems such as ionic interactions, low reactant concentration, and the difficulty in removing stabilizers. Quaternary ammonium salts used for stabilizing metal nanoparticles were proposed by Bonnemann and the particles are not dispersible in water because the anionic surface of particles is surrounded by the hydrophobic tetraoctyl quaternary ammonium ions [Bonnemann et al., 1991]. Furthermore, the preparation of nanoparticles of noble metals in water to diameter of lower than 5 nm has been difficult by conventional stabilization with polymers or surfactants.

In the present work, thiol-functionalized imidazolium ionic liquids (TFILs) were adopted as stabilizers for preparing Pd nanoparticles. In the previous report, we indicated that the TFILs could effectively form Au and Pt nanoparticles [Kim et al., 2004b]. Subsequently, Itoh et al. used the TFILs to prepare Au nanoparticles and also showed that the hydrophilic and hydrophobic properties of Au nanoparticles could be tuned by exchanging of anions in the IL moiety [Itoh et al., 2004]. The TFILs could be good candidates as stabilizers based on the following theoretical background: (1) The cation and anion of the IL can be tailored by thiol substitutes as shown in Scheme 1. The nanoparticles that are passivated by thiol group are readily and stably dispersible in solvents. (2) The ILs can be easily manufactured as hydrophobic or hydrophilic liquids by modifying their structure. The TFILs are therefore soluble in organic solvents or aqueous media for the preparation of nanoparticles. (3) The ILs are liquids that consist of ions. The solvation of species of ionic transition metals such as the Pd and Pt salts in the TFILs should be favored much more than one in conventional solvents. (4) After synthesis, the TFILs are easily separated from the nanoparticle products by the difference in solubility. These intrinsic properties make the TFILs efficient stabilizers for the formation and stabilization of nanoparticles in both aqueous and nonaqueous solutions.

Particularly, in this study we report on the synthesis of the TFILs and their use in the preparation of Pd nanoparticles. We also use

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**Scheme 1. The reaction mechanism for the synthesis of TFIL-3.**

transmission electron microscope (TEM) images to analyze the size distribution of the prepared nanoparticles.

## RESULTS AND DISCUSSION

### 1. Synthesis of TFIL-3

Scheme 1 shows the reaction mechanism for the synthesis of TFIL-3. It was found that the  $^1\text{H}$  NMR spectra of synthesized IL were consistent with the previous results [Kim et al., 2004b]. We synthesized the TFIL-3 as follows. First, the 1,3-di(2,3'-dihydroxypropyl)imidazolium chloride was prepared from imidazole and 3-chloro-1,2-propanediol using standard procedures [Dubreuil et al., 1999]. The resulting yield appeared to be 91%. A mixture containing 0.1 mol of 1,3-di(2,3'-dihydroxypropyl)imidazolium chloride and 0.4 mol of mercaptoacetic acid was then refluxed with 0.04 mol of tosylisocyanate (TsOH) in toluene. The product was 1,3-di(2,3'-dimercaptoacetoxypropyl)imidazolium chloride (TFIL-2) and the yield was 72%. The 0.05 mol of the TFIL-2 and 0.05 mol of sodium 3-mercaptopropanesulfonate (Na-MPA) were dissolved in hot water ( $60^\circ\text{C}$ ) and was stirred for 24 h. The product was 1,3-di(2,3'-

dimercaptoacetoxypropyl)imidazolium, 3''-mercaptopropanesulfonic acid (TFIL-3) and the yield was 60%. ( $\text{D}_2\text{O}$ , 500 MHz, TMS)  $\delta$  2.26-2.33 (t, 5H, SH); 2.90-3.08 (m, 6H,  $\text{CH}_2$ ); 3.43-3.72 (d, 8H,  $\text{CH}_2\text{COO}$ ); 3.73-3.76 (d, 4H, N- $\text{CH}_2$ ); 4.10-4.11 (s, 3H,  $\text{NCH}_3$ ); 4.39-4.56 (m, 2H, CHO; d, 4H,  $\text{CH}_2\text{O}$ ); 7.52-7.75 (d, H, H-4); 7.81-7.91 (d, H, H-5); 8.98-9.03 (d, H, H-2).

### 2. Preparation of Pd Nanoparticles

The use of TFIL-3 in the one-phase preparation of Pd nanoparticles was straightforward and the purification of nanoparticles was carried out in ambient condition. The 0.1 mmol of TFIL-3 in 10 ml of water was added dropwise under vigorous stirring to a solution of 0.1 mmol of sodium tetrachloropalladate in 10 ml water. The reaction mixture produced a slightly turbid dispersion because of the formation of metal-sulfide group bonding. After the mixture had been stirred for approximately 30 min at room temperature, 0.1 mmol of a freshly prepared aqueous solution of sodium borohydride ( $\text{NaBH}_4$ ) in water was added dropwise under vigorous stirring. We continued to add a reducing agent until no gas evolution was observed, at which time the reduction was completed. We found no precipitates in the dispersions, and the dispersions were stable for several weeks.

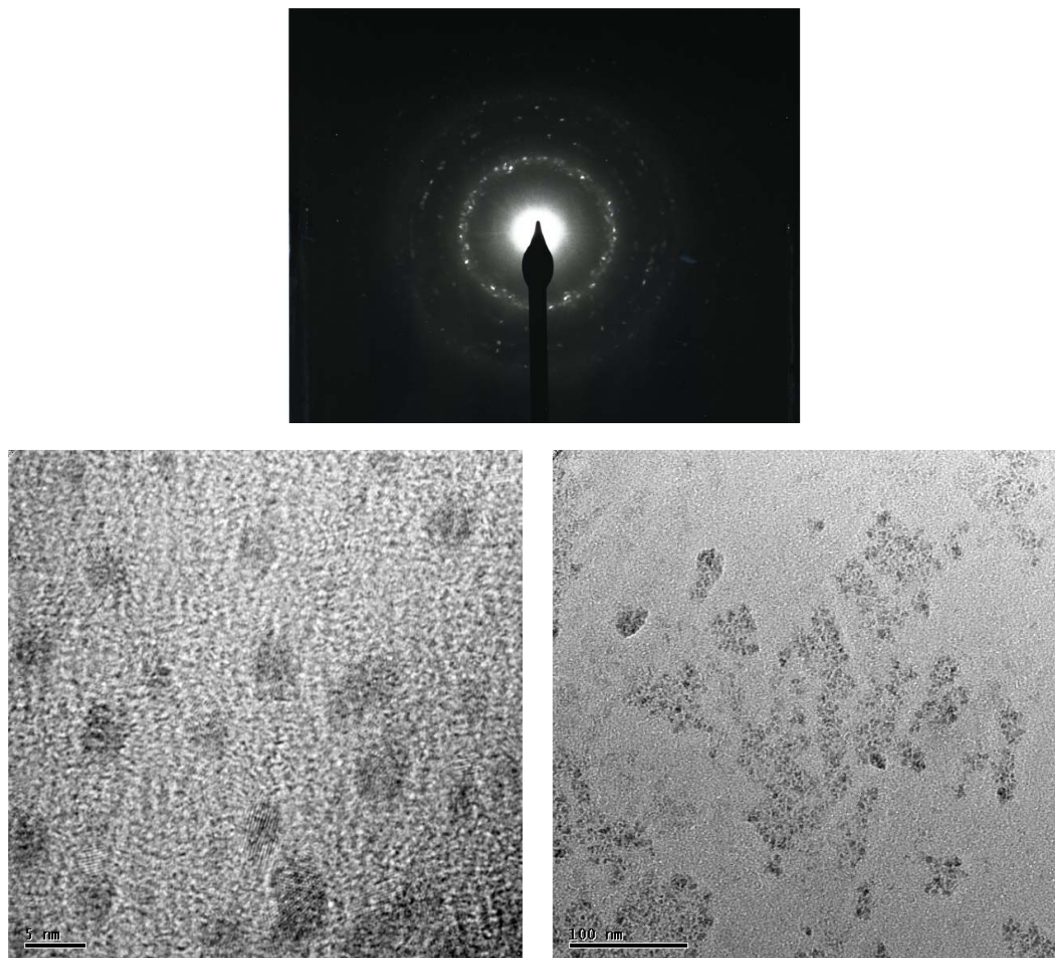


Fig. 1. Electron diffraction and TEM images of the Pd nanoparticles stabilized by TFIL-3.

The stabilized Pd nanoparticles were then purified to remove the excess of unbounded ionic liquid stabilizer molecules which are soluble in alcohol. From this process we produced a powder form of Pd nanoparticles. After precipitating nanoparticles and removing supernatant liquid, we then dried nanoparticles in a vacuum oven (0.04 Torr) at room temperature. Finally, the purified Pd nanoparticles could be kept in powder form or redispersed in water.

### 3. Analysis

TFIL-3 (1,3-di(2',3'-dimercaptoacetoxypropyl)imidazolium, 3''-mercapto-1''-propanesulfonic acid) as a stabilizer for preparing palladium (Pd) nanoparticles was synthesized. The  $^1\text{H}$  spectra were recorded on a Bruker AMX FT 500 MHz NMR spectrometer. The NMR spectra, which had already been checked in a recent report, were in accord with the presence of TFIL-3. This IL was designed to have five thiol groups on the positions of cation and anion as well as on symmetrical positions in cation as shown in Scheme 1.

Thin films of nanoparticle solution in water were drop cast onto a 300 mesh carbon-supported film copper grid. To obtain bright field images and normal incidence selected area electron diffraction (SAED) patterns, we used a Phillips CM-120 high-resolution transmission electron microscope (HRTEM) with a beam energy of 200 keV. From these images and patterns, we could determine the average particle size and distribution. Figs. 1 and 2 show the

TEM images and size distribution, respectively, for the crude nearly spherical Pd nanoparticles. Our estimates of average particle size were based on the measurements of 200 particles from random regions. The histogram shows average diameter was 3.0 nm and the

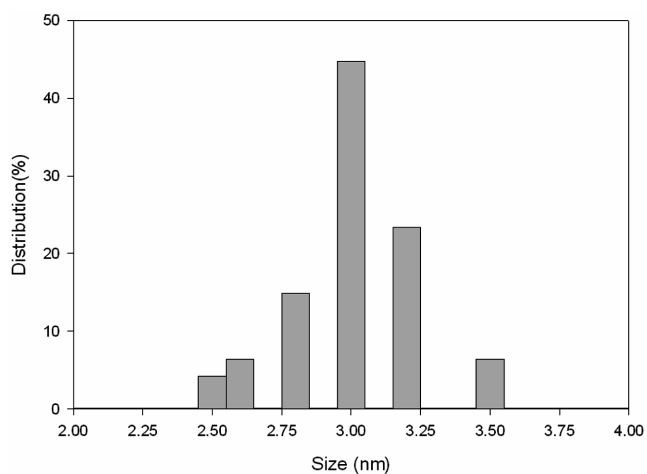


Fig. 2. Size distribution of the Pd nanoparticles stabilized by TFIL-3.

standard deviation was 0.15 nm. A representative detailed section of the image in Fig. 1 further corroborates the crystalline nature of these metal nanoparticles. Electron diffraction reveals that all Pd nanoparticles are crystalline with face-centered cubic (fcc) packing arrangements of bulk metals.

In the previous study [Kim et al., 2004b] we revealed that the metal nanoparticles stabilized by the TFIL, which has thiol groups on the cation and the anion as well as on symmetrical positions in cation, display a small average particle size and a narrow distribution. The TEM images show how small and mono-dispersed spherical nanoparticles were prepared and suggest that the number of thiol groups in the TFIL considerably affects the size and the stability of Pd nanoparticles. The TFIL, which is believed to use an electrostatic and steric method of protection to stabilize Pd nanoparticles in aqueous solutions, effectively prevents the formation of larger Pd aggregates. In addition, the structure and species of IL and the chemical and physical interaction between TFIL and metal are decisive in preparing metal nanoparticles. Moreover, the powder nanoparticles can be readily and stably dispersed into water without producing flocculates or precipitates.

### CONCLUSION

We have demonstrated the synthesis of TFIL (1,3-di(2',3'-dimer-captoacetoxypopyl)imidazolium, 3''-mercapto-1''-propanesulfonic acid) as well as one-phase preparation of TFIL-stabilized Pd nanoparticles. Transmission electron microscopy (TEM) showed the average diameter and standard deviation of Pd nanoparticles to be 3.0 nm and 0.15 nm, respectively. The thiol functional groups in the IL act as selective media that control the size and uniformity of the Pd nanoparticles. Further investigations with respect to the effects of the number of thiol groups and the species and structure of cations and anions in IL on the formation of metal nanoparticle are required for better understanding of the IL-based nanoparticle preparation. The structural design and tuning of the ILs and the combination of the ILs and thiol groups can improve the preparation of size-selective nanomaterials more effectively than conventional methods.

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### NOMENCLATURE

IL : ionic liquid  
Pd : palladium

TFIL : thiol-functionalized ionic liquid  
TEM : transmission electron microscopy

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